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Light emission in reverse bias operation from poly(3-octylthiophene)-based light emitting diodes

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We report light emission from light emitting diodes with poly(3-octylthiophene) (P3OT) as the active layer in both forward and reverse bias operation. The onset of electroluminescence (EL) of ITO/P3OT/Al devices occurs at current densities of 6.25×10^{-4} A/cm^2 in both modes of operation; both cases show identical EL spectra. For a P3OT thickness of 100 nm the onset of electroluminescence and current occurs at 3 V in the forward bias mode, and at about 18 V in the reverse mode of operation, at which a completely different voltage dependence of the current is observed. In the reverse mode of operation, the data suggest that carrier injection is a tunneling process through a triangular barrier of 0.4 eV at the metal–polymer interface. In the forward bias a Schottky-like behavior is seen. © *1995 American Institute of Physics.*

Since the first reports on electroluminescence from conjugated semiconducting polymers,[1,2] a new field of research has opened up, largely stimulated by the interest from industry to use these materials as active components in various display applications. Although much progress has been made in understanding the basic principles of operation of these devices, many questions remain unanswered, especially regarding the transport properties and their relation to the amorphous, disordered nature of conjugated polymers. One of the fundamental questions to be addressed is whether these materials can be modeled in a standard semiconductor bandlike picture. The validity of such a bandlike model is the subject of current debate.[3,4]

In spite of the basically ''simple'' approaches underlying the presently popular band model (clean band gap without traps, no Fermi-level pinning at the interfaces with metal contacts), the model seems to work quite well to describe most electrical properties and light emission of light emitting diodes (LEDs).[5] In forward bias conditions, injection of electrons into the conduction band from a low work-function electrode and injection of holes into the valence band from a high work-function electrode [see Fig. 1(a)] would allow the recombination of excitations formed from opposite charge carriers, which causes electroluminescence. Within this approach, one might expect electroluminescence to occur also under extreme reverse bias conditions. In this case, electrons would then tunnel from the high work-function electrode into the conduction band, and holes from the low work-function electrode into the valance band. While in the forward mode of operation various mechanisms of charge injection (thermionic emission, tunneling) can play a substantial role within such a picture, tunneling of charge carriers should be the dominant injection mechanism in the reverse mode of operation [see Fig. 1(b)]. In this paper we report for the first time light emission from conjugated polymer LEDs operated in forward as well as in reverse bias, while entirely different voltage dependencies of the currents are observed in both modes.

To study light emission we have focused on poly(3-octylthiophene), the homopolymer from a complete series of materials in which color tuning over the entire visible regime has been reported.[6] The polymer was prepared according to a regioselective polymerization procedure;[7] the desired regioselectivity was confirmed by ^{1}H NMR spectroscopy. The polymer was purified by repeated precipitation prior to use. Devices were made by spin coating the polymer from toluene solution (5% by weight) onto ITO-covered glass slides. Since the quality of the ITC-polymer contact is very important for homogeneous and stable devices, special attention was paid to a cleaning procedure for the ITO surface prior to spin coating, based on ultrasonification in polar and nonpolar solvents. After spin coating (rates varying from 500–4000 rpm), metal contacts of aluminum were vacuum evaporated at pressures below 10^{-6} mbar and evaporation rates below 1 nm/s, to avoid unnecessary heating of the polymer top layer. Several electrodes were contacted in a sample holder with gold spring contacts; electrode areas varied from 8 to 24 mm^2 within one sample. Film thicknesses were determined

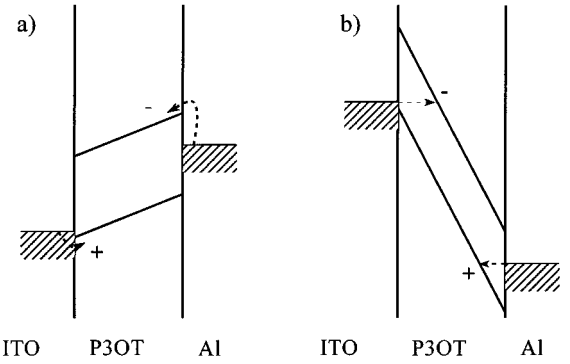

FIG. 1. Band image of an ITO/P3OT/Al device, based on well-known values for the metal work functions of ITO and Al (4.7 and 4.3 eV, respectively) and the poly(3-octylthiophene) energy gap of 2.1 eV. (a) Forward bias (+ on ITO, − on Al) and (b) reverse bias (+ on Al− on ITO).

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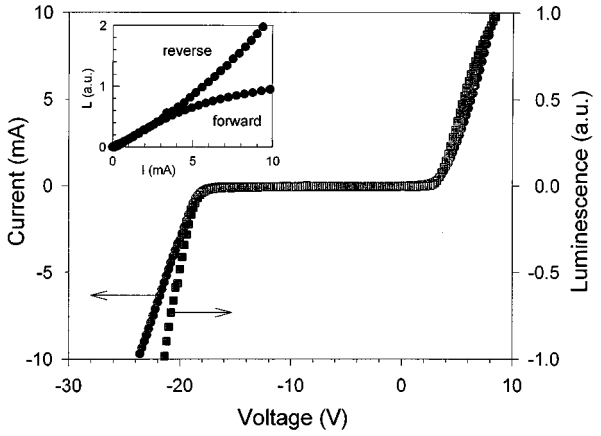

FIG. 2. Current-voltage (circles) and electroluminescence-voltage (squares) characteristics of a 100 nm thick ITO/P3OT/Al LED under forward and reverse bias. The total device area is 8 mm^2. In forward bias the positive voltage is on ITO, the negative on Al. The inset shows the dependence of EL on forward and reverse bias currents.

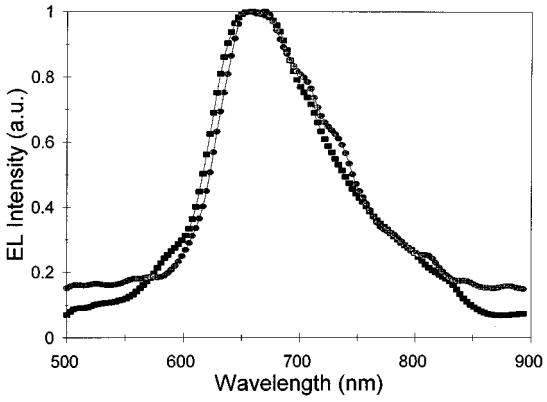

FIG. 3. Electroluminescence spectra of P3OT LEDs under forward (squares) and reverse (circles) bias, taken at +8 and −20 V, respectively.

with a Dektak surface profiler. I–V measurements were taken with a Keithley 236 SMU operated in pulsed mode (duty cycle 20%) to reduce heating effects. Light detection was performed with a calibrated photodiode mounted on an integrating sphere to obtain values for the external quantum efficiency of the devices. All measured diodes in a batch of 8 samples showed the reported behavior (light emission in both forward and reverse mode of operation) with comparable quantum efficiencies. From subsequent measurements of one diode characteristic we note that the I–V characteristics are reproducible, although the efficiency of the devices decreases as a function of time. The exact shape of the I–V characteristics depends strongly on sample preparation (cleaning steps, filtering, evaporation conditions) and can be entirely different for a different batch of samples.

In Fig. 2 the luminescence and current versus voltage are shown for an ITO/P3OT/Al device (the polymer thickness is 100 nm, the total area of the device is 8 mm^2). The device acts as a diode, showing large forward currents above 3 V (forward is defined as the positive voltage on ITO) and very small currents at the corresponding reverse voltages. Rectification ratios as high as 10^4 have been obtained. In forward and reverse bias, light emission is observed as soon as the current is higher than 6.25×10^{-4} A/cm^2; this condition is met at entirely different electric fields in both modes of operation. This suggests that the onset of light emission depends on the amount of current flowing through the device and not on the value of the electric field. The data taken under forward bias suggest (thermionic) emission over a Schottky-like barrier of 0.69 eV to be the dominant injection mechanism for electrons at the polymer–Al contact; this assignment is supported by C–V measurements.

From Fig. 2 we see that the luminescence and the current have a similar dependence on the voltage across the device, in forward and in reverse bias mode. For voltages corresponding to current densities below 0.1 A/cm^2, the luminescence is proportional to the current through the device, while at higher voltages reproducible deviations (superlinear in reverse, sublinear in forward mode) from the linear behavior are observed. These effects are indicated in the inset of Fig. 2. The recombination rates for charge carriers with species of the opposite charge strongly depends on the density of available charge carriers, which is mostly determined by the heights of the two injection barriers. The data in the inset of Fig. 2 suggest that in the reverse mode of operation the injection is a more balanced process, since the light output is higher at the same current density as under forward bias operation. This picture is consistent with the assumption that in reverse mode of operation two barriers dominate the injection mechanism, while in forward mode of operation only the electron-injecting contact limits the total light output (see Fig. 1).

In reverse bias operation the only possible mechanism for injection into the valence and conduction bands of the polymer is by direct tunneling through the triangular barrier formed at the metal–polymer interface. In Fig. 1(b) we indicate that for a current to flow in the reverse mode the ITO has to be the electron injector, while Al takes over the role of hole injector. Field-driven Fowler–Nordheim tunneling of electrons or holes through a triangular barrier gives[5]

$$I \propto E^2 \exp \frac{-\kappa}{E}, \tag{1}$$

$$\kappa = \frac{4(2m^*)^{1/2}}{3\hbar e}\,\phi^{3/2}, \tag{2}$$

where E is the electric field, m^* is the effective mass of the charge carrier (m^* is here taken to be the free electron mass), and ϕ is the barrier height. The barrier height obtained from Fowler–Nordheim analysis is 0.4 eV. Since two types of charge carriers are involved in the measured current, it is difficult to determine which of the two barriers is the highest. From a geometric argument, both barriers are expected to play a significant role in reverse mode operation.

Electroluminescence spectra of the devices in both modes of operation were recorded with an SLM-500 Aminco spectrofluorometer. As can be seen in Fig. 3 the EL spectra (not corrected for the spectral sensitivity of the detector) in forward (+8 V) and reverse (−20 V) mode of operation are quite similar, implying that the origin of electric field driven luminescence is the same. This is in agreement with the concept that two types of charge carriers are needed to form an

excited state that can decay radiatively, independent of the way in which those charge carriers are injected. It is a well-known fact that breakdown of organic LEDs is accompanied with some kind of plasma emission, usually associated with broadened electroluminescence spectra, especially in the high wavelength regime. This breakdown situation was not reached in this case in either forward or in reverse modes, as could be seen either by eye or from the electroluminescence spectra of Fig. 3.

In summary, we have shown for the first time light emission from conjugated polymer LEDs in both forward and reverse modes of operation. Although the dominant injection mechanism of charge carriers is different in both regimes, the absolute current determines the onset of luminescence, independent of the electric field needed to reach this situation. Fowler–Nordheim tunneling of electrons into the conduction and holes into the valence band of poly(3-octylthiophene) is proposed as the dominant injection mechanism under reverse bias, while in forward operation Schottky-like behavior is observed. At current densities below 0.1 A/cm^2, the luminescence depends linearly on the current in both modes of operation.

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